X-Ray Crystallography

Prof. R. K. Ray
MN Dastur School of Materials Science and Engineering
Indian Institute of Engineering Science and Technology, Shibpur
Department of Metallurgical and Material Engineering
Indian Institute of Technology, Madras

Lecture - 25
Chemical Analysis by X-Ray Absorption

We have already seen that, when a primary beam of X-rays is incident on a sample. It can produce secondary X-rays in the form of fluorescent k characteristic radiations. Since, the characteristic radiations are very much characteristics of the element concerned therefore based on this phenomenon there is a chemical analysis method that has been devised. That is known as chemical analysis by X-ray fluorescence.

Now, when a material is used as an absorber of X-rays we have seen that if the intensity of the transmitted beam through the absorber is measured for bombardment by a large number of monochromatic waves of X-rays. Then, for any particular material a characteristic edge, absorption edge wavelength is obtained; as shown over here.

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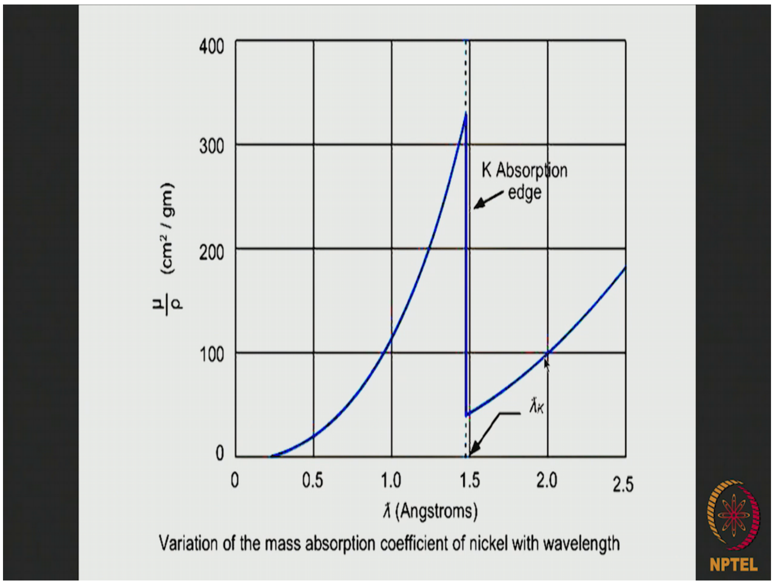

Variation of the mass absorption coefficient of nickel with wavelength

So, this is the variation of the mass absorption coefficient of nickel with wavelength when you bombard the strip of nickel with various wavelengths; a large number of wavelengths. Then for this particular element nickel we find that there is what is known a k absorption edge wavelength here, which demarked between region high absorption and region of low absorption. Now the k absorption edge wavelength is very much a characteristic of the absorbing element.

So, based on this phenomenon another chemical analysis method has been devised known as chemical analysis by X-ray absorption. In this method if we have a number of elements in a sample when it is bombarded with monochromatic wavelengths of different values then it is quite possible that the k absorption edge wavelengths of the different elements present in the sample will be disclosed. And by identifying those k absorption edge wavelengths it is possible to identify the elements present within the sample.

Now the process can be done in a diffractometer in the following manner.

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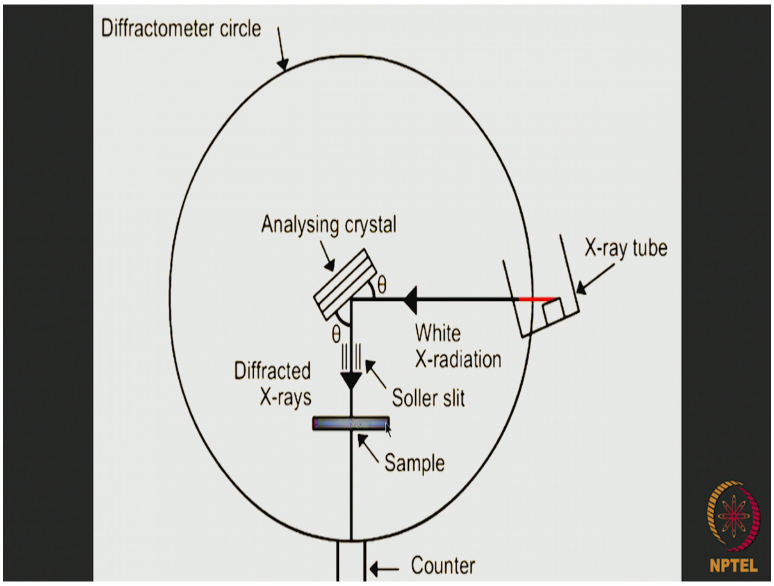

Say we have an X-ray tube here which produces both white radiation and characteristic radiation. Now this white radiation is allowed to fall on an analyzing crystal, and depending on the interlunar distances of the planes which lie parallel to the surface of the analyzing crystal, and the angle of incidence, and the wavelengths certain wavelength will from the white radiation will be diffracted. Following Bragg’s condition of diffraction lambda is equal to 2 d sin theta. Now that particular wavelength is allowed to pass through the sample and the transmitted intensity is recorded.

So, we do it for a large number of wavelengths to be incident on the sample, and in each case we measure the transmitted intensity. Then from the values of the transmitted intensities versus the wavelengths that are incident on the sample we can find out the precise value of the k absorption edge wavelength or k absorption edge wavelengths. There is another method which is also used..

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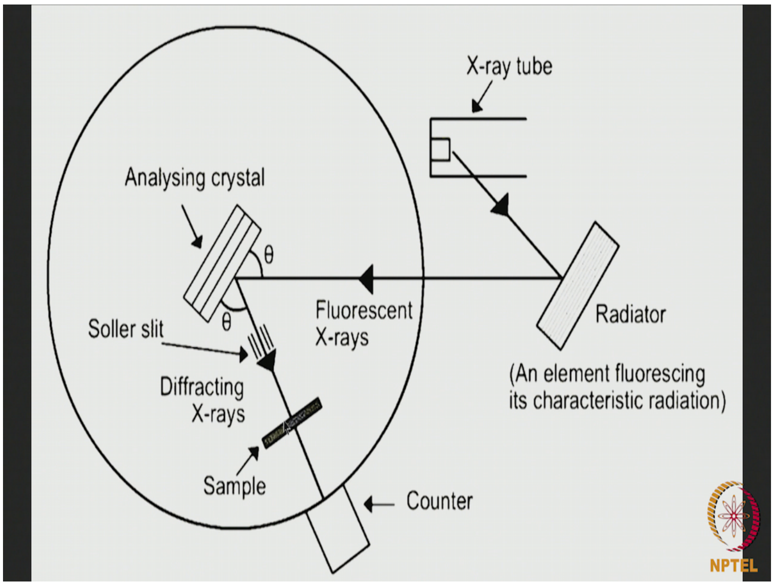

Here, from the X-ray tube the primary X-ray beam is allowed to fall on a radiator. Radiator is nothing but an element which fluoresces its characteristic radiation by the impact of the primary X-ray beam.

Now, this fluorescent radiation is allowed to fall on the analyzing crystal and if the single wavelength fluorescent radiation it will be diffracted at a particular setting of the angle theta. And that is allowed to fall on the sample and the transmitted intensity is recorded in the counter. So, if we have a large number of elements having atomic number z z plus 1 z plus 2 z plus 3 etcetera, etcetera and if these are used as radiators, then we will have fluorescent x radiation of different wavelength. And these will be allowed to fall on the analyzing crystal and finally on the sample one after the other. So, in this way also we can plot transmitted intensity versus theta card for the sample.

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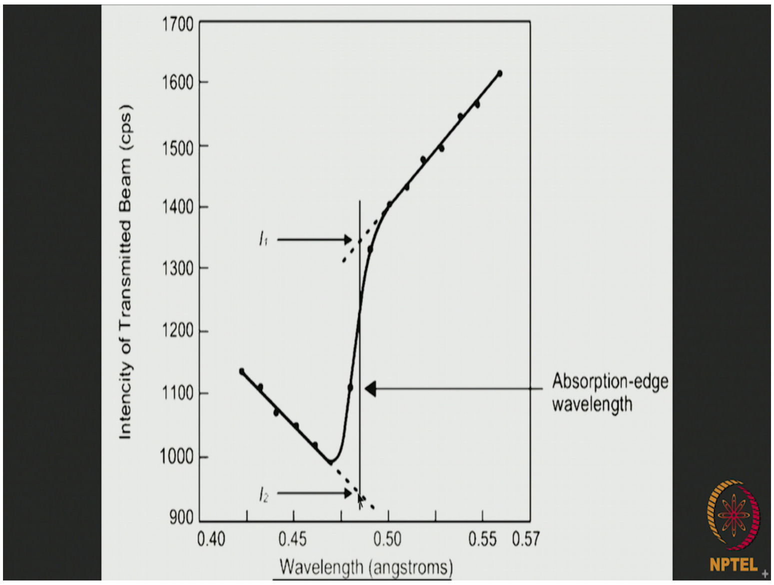

Now, once we do that this is a type of plot we obtain this intensity of the transmitted beam and this is the wavelength of the incident radiation. Now as you can see there will be a gradual decrease in the intensity of the transmitted beam as the wavelength becomes shorter and shorter and then there will be an abrupt change indicating that the k absorption edge wavelength is here. Now if we extrapolate these two parts of the curves and allow it to lie intersect the k absorption edge wavelength then this intensity is the intensity just to the right of the absorption edge and this intensity over here represents the intensity just to the left of the k absorption edge wavelength.

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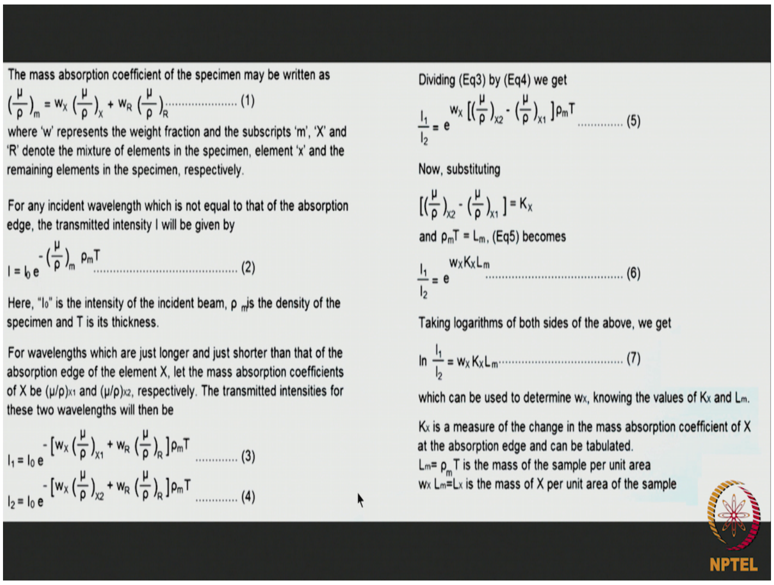

The mass absorption coefficient of the specimen may be written as

$$\left(\frac{\mu}{\rho}\right)_m = w_X \left(\frac{\mu}{\rho}\right)_X + w_R \left(\frac{\mu}{\rho}\right)_R \quad \ldots\ldots\ldots\ldots (1)$$

where 'w' represents the weight fraction and the subscripts 'm', 'X' and 'R' denote the mixture of elements in the specimen, element 'x' and the remaining elements in the specimen, respectively.

For any incident wavelength which is not equal to that of the absorption edge, the transmitted intensity I will be given by

$$I = I_0 e^{-\left(\frac{\mu}{\rho}\right)_m \rho_m T} \quad \ldots\ldots\ldots\ldots (2)$$

Here, "I_0" is the intensity of the incident beam, ρ_m is the density of the specimen and T is its thickness.

For wavelengths which are just longer and just shorter than that of the absorption edge of the element X, let the mass absorption coefficients of X be $(\mu/\rho)_{x1}$ and $(\mu/\rho)_{x2}$, respectively. The transmitted intensities for these two wavelengths will then be

$$I_1 = I_0 e^{-\left[w_X \left(\frac{\mu}{\rho}\right)_{X1} + w_R \left(\frac{\mu}{\rho}\right)_R\right]\rho_m T} \quad \ldots\ldots\ldots\ldots (3)$$

$$I_2 = I_0 e^{-\left[w_X \left(\frac{\mu}{\rho}\right)_{X2} + w_R \left(\frac{\mu}{\rho}\right)_R\right]\rho_m T} \quad \ldots\ldots\ldots\ldots (4)$$

Dividing (Eq3) by (Eq4) we get

$$\frac{I_1}{I_2} = e^{w_X \left[\left(\frac{\mu}{\rho}\right)_{X2} - \left(\frac{\mu}{\rho}\right)_{X1}\right]\rho_m T} \quad \ldots\ldots\ldots\ldots (5)$$

Now, substituting

$$\left[\left(\frac{\mu}{\rho}\right)_{X2} - \left(\frac{\mu}{\rho}\right)_{X1}\right] = K_X$$

and $\rho_m T = L_m$, (Eq5) becomes

$$\frac{I_1}{I_2} = e^{w_X K_X L_m} \quad \ldots\ldots\ldots\ldots (6)$$

Taking logarithms of both sides of the above, we get

$$\ln \frac{I_1}{I_2} = w_X K_X L_m \quad \ldots\ldots\ldots\ldots (7)$$

which can be used to determine w_x, knowing the values of K_x and L_m.

K_x is a measure of the change in the mass absorption coefficient of X at the absorption edge and can be tabulated.
$L_m = \rho_m T$ is the mass of the sample per unit area
$w_x L_m = L_x$ is the mass of X per unit area of the sample

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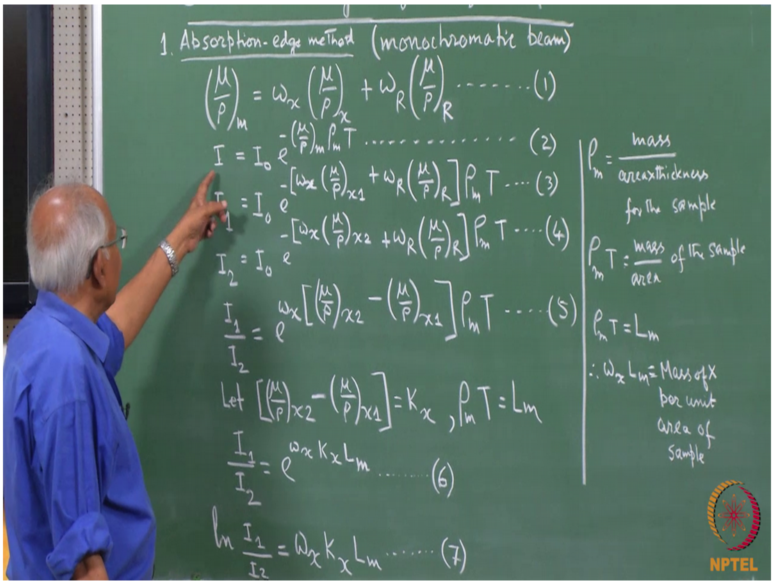

1. Absorption-edge method (monochromatic beam)

$$\left(\frac{\mu}{\rho}\right)_m = \omega_x \left(\frac{\mu}{\rho}\right)_x + \omega_R \left(\frac{\mu}{\rho}\right)_R \quad \cdots\cdots (1)$$

$$I = I_0 e^{-\left(\frac{\mu}{\rho}\right)_m \rho_m T} \quad \cdots\cdots (2)$$

$$I_1 = I_0 e^{-\left[\omega_x \left(\frac{\mu}{\rho}\right)_{x1} + \omega_R \left(\frac{\mu}{\rho}\right)_R\right] \rho_m T} \quad \cdots (3)$$

$$I_2 = I_0 e^{-\left[\omega_x \left(\frac{\mu}{\rho}\right)_{x2} + \omega_R \left(\frac{\mu}{\rho}\right)_R\right] \rho_m T} \quad \cdots (4)$$

$$\frac{I_1}{I_2} = e^{\omega_x \left[\left(\frac{\mu}{\rho}\right)_{x2} - \left(\frac{\mu}{\rho}\right)_{x1}\right] \rho_m T} \quad \cdots (5)$$

Let $\left[\left(\frac{\mu}{\rho}\right)_{x2} - \left(\frac{\mu}{\rho}\right)_{x1}\right] = K_x$, $\rho_m T = L_m$

$$\frac{I_1}{I_2} = e^{\omega_x K_x L_m} \quad \cdots\cdots (6)$$

$$\ln \frac{I_1}{I_2} = \omega_x K_x L_m \quad \cdots\cdots (7)$$

$\rho_m = \frac{\text{mass}}{\text{area} \times \text{thickness}}$ for the sample

$\rho_m T = \frac{\text{mass}}{\text{area}}$ of the sample

$\rho_m T = L_m$

$\therefore \omega_x L_m =$ Mass of X per unit area of sample

Now based on the disclosure of absorption edge wavelengths there has been a method for chemical analysis and this is known as the absorption edge method and here as I have already explained monochromatic X-ray beam is used. Now if in the material we have got an element x and the rest of the elements are represented as R we can write down for the mixture mu by rho m is equal to W x mu by rho x plus W R mu by rho R W x is the weight fraction of x W R is the weight fraction of R and mu by rho is the mass absorption coefficient here it is the mass absorption coefficient for x and this is mass absorption coefficient for R. Now we can write down the transmitted intensity I as equal to I 0 the incident intensity into e to the power minus mu by rho m for the mixture rho m the density of the mixture into t the thickness of the sample.

If we considered intensities I 1 and I 2 here then we can also write down I 1 in this manner I 1 will be I 0 the incident intensity to e to the power minus W x mu by rho x one that indicates that we are considering the intensity I 1 at that level plus W R mu by rho R rho m t whereas, I 2 can be written as I 0 e to the power minus W x v by rho x 2 this corresponds to the transmitted intensity I 2 plus W R mu by rho R rho m t. Now if we divide I 1 by I 2 it becomes e to the power W x mu by rho x 2 minus mu by rho x one multiplied by rho m into t let this quantity here be written as k subscript x and let rho m t here be written as l m.

If that be the case we can rewrite I 1 by I 2 as e to the power W x k x l m taking logarithm of both sides we can write down l n I 1 by I 2 is equal to W x k x l m. So, from this equation its quite clear that this part of the left hand side is a measurable quantity l n I 1 by I 2 k x can also be determined the mu by rho value at the 2 different places and l n is rho m into t the density and the thickness. So, that can also be measured so that from this equation we can easily find out the weight fraction of x. So, this method is known as the absorption edge method for chemical analysis. Now here row m is a density of the mixture.

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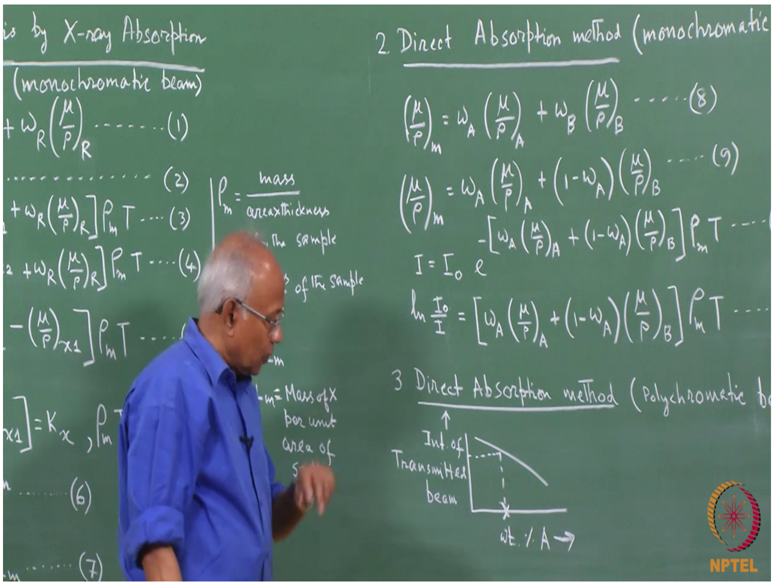

So, rho m is nothing but mass of the mixture of mass of the substance divided by its area into thickness mass per unit volume this is for the sample. So, if we multiply by t then it will be simply mass per area of the sample. Now rho m t has been written as l subscript m. So, if we write W x multiplied by l m it is actually mass of x per unit area of the sample. Now the second method based on absorption of X-rays is known as the direct absorption method. Now here also we use a monochromatic beam of X-rays. So, here the chemical allowances done considering the direct absorption.

Here we do not look for the absorption edge wavelengths, but we measure it find out the chemical composition chemical analysis on element directly from how much of the radiation is absorbed by the sample again we can write down for the sample mu by rho m is equal to W a mu by rho a plus W B mu by rho B where a and B are the elements which are present in the sample. So, since there is nothing else is present then W B is nothing but 1 minus W a because W a the weight fraction of a plus W B the weight fraction of B must be equal to 1. So, we can write mu by rho n is equal W a mu by rho a plus 1 minus W a mu by rho B therefore, we can write the transmitted intensity I is equal to incident intensity I 0 e to the power minus W a mu by rho a plus one minus W a mu by rho B rho m t.

Where rho m is the density of the sample and t is the thickness of the sample taking logarithm of both sides and then or taking the logarithm of I 0 by I rather we get l n I 0 by I will be W a mu by rho a plus 1 minus W a mu by rho B rho m t. Now here mu by rho of A and B are known quantities rho m and t are also known. So, the only unknown is W A and on the left hand side these are measurable quantities. So, from this equation W a or weight fraction of a can be easily found out there is still a third absorption method which is used for chemical analysis and that is known as direct absorption method polychromatic beam.

You see when we deal with monochromatic beam the chances of having an intense beam is much less and after absorption when we measure the transmitted intensity it may be very difficult to do. So, that is the reason why in some method we use what is known as the direct absorption method polychromatic beam; that means, here we use the white radiation that comes out from the X-ray tube along with the characteristic radiation, but in this case we cannot set up these equations because we do not know which component of the polychromatic beam is passing through the sample.

In fact, the setup in this case is we put the sample along the polychromatic beam to fall on the specimen from the X-ray tube on the other side we have the counter to record the transmitted beam. So, in this cases where we are not we do not we cannot rather find out which particular wavelength is getting transmitted we do it in a different way we draw a calibration curve with x axis intensity of the transmitted beam how much is getting transmitted and weight percent of A along the x axis; that means, we take a large number of samples where the weight fractions of the other elements are fixed and weight fraction of a changes.

So, several samples with different weight fractions of A; we prepare and for each we undertake this experiment of polychromatic beam falling on a certain thickness of the sample and getting transmitted through it and getting recorded with a counter. So, if we do this experiment for a large number of samples where only the percentage or the weight fraction of A differs everything else remains the same then you can easily draw a calibration curve of intensity of transmitted beam versus weight percent A from the several samples. Now if we have an unknown sample where weight percent of A is not known then it is simply a question of finding out what is the transmitted intensity.

And then from this calibration curve we can easily find out what is the weight fraction of A in the unknown sample. Now to be of any practical use we have to remember that you know you have the polychromatic beam from the same X-ray machine under similar condition to be incident on the different samples with different weight fraction of A not only that the thicknesses of the different samples must be strictly the same then and then only this method will be successful. Now one of the application of know the X-ray absorption is where we study diffusion you see in diffusion couple experiments this kind of experiments are very useful.

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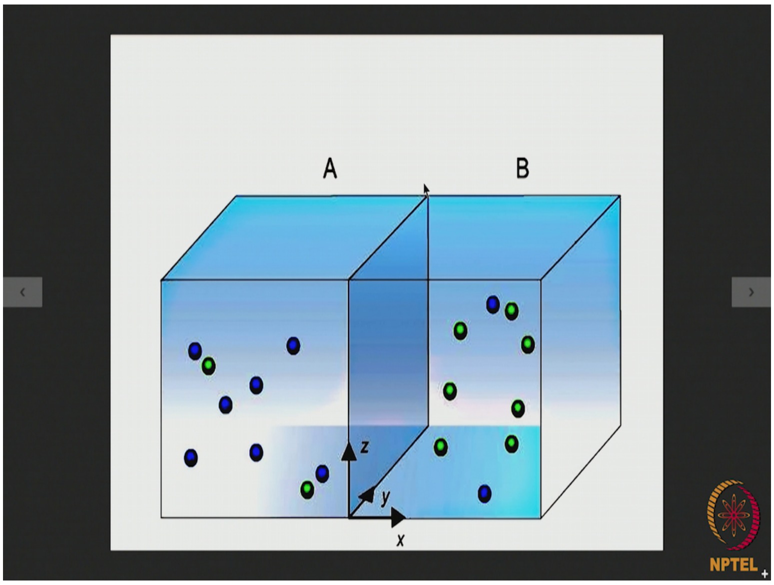

Say for example, we have got 2 metals A and B join together over here and this diffusion couple if it is kept at a sufficiently high temperature for quite some time what will find that atoms of A will move over to B they will diffuse to be similarly atoms of B will diffuse and move over to A. So, when a steady state condition will be reached we should be able to figure out how the concentration of A varies from as a function of the distance x and how the concentration of B varies as a function of the distance x.

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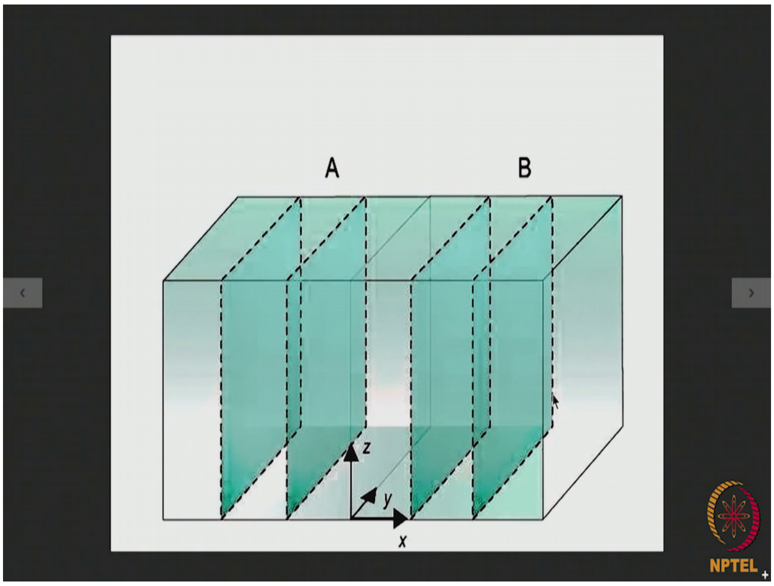

Now, the way it is done is this say for example if we take slices parallel to the y z section at different values of x and then use those samples for the analysis of concentration of A and concentration of B then from that data. We can draw curves for the concentration of A versus x and concentration of B versus x well using this X-ray absorption method.

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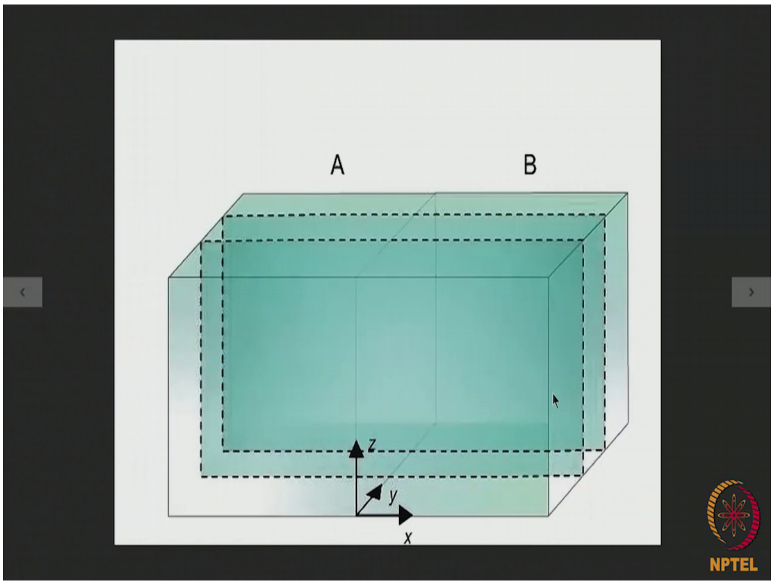

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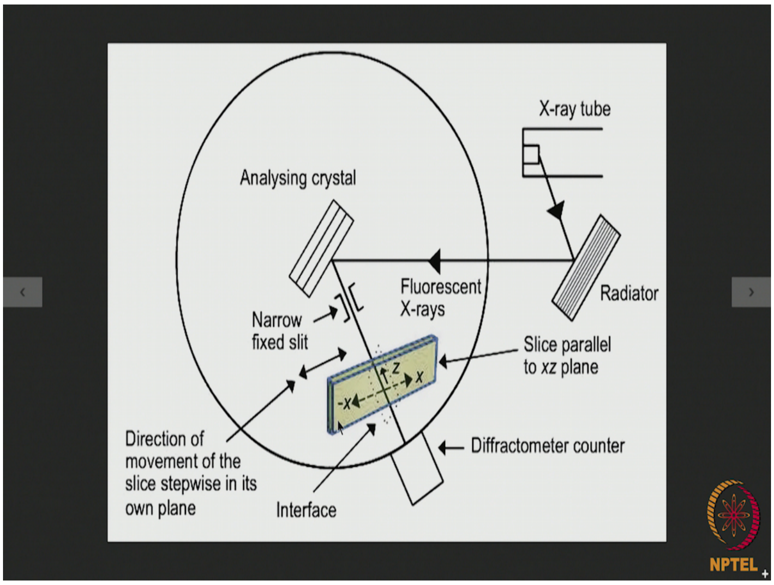

We can do it on a single section say for example, in this diffusion couple if we take a section like this which is in the this section which is in the x z section actually is parallel to the x z section we cut a single slice from here after the materials have diffused and then we use this as the sample in a diffractometer in this manner where we have X-rays primary X-rays incident on a radiator and the fluorescent beam falls on analyzing crystal and a monochromatic beam falls over here and if this sample is given movement in negative x and negative y and if the slit is rather narrow then as a function of x, we can find out what are values of concentration of A and concentration of B.

So, what is done you know the sample is kept in a particular position for sufficiently long time. So, that sufficient transmitted intensity is obtained here then the sample is moved say slightly towards the right and again this X-ray narrow X-ray beam is allowed to fall over there and we get the transmitted intensity if this is done at several places along plus x and minus x then from those using those equations here we can find out what are the concentrations of A and B atoms as a function of x and then we can plot it in this fashion. So, we will see that concentration of A will vary in this fashion and concentration of B will vary in this fashion.

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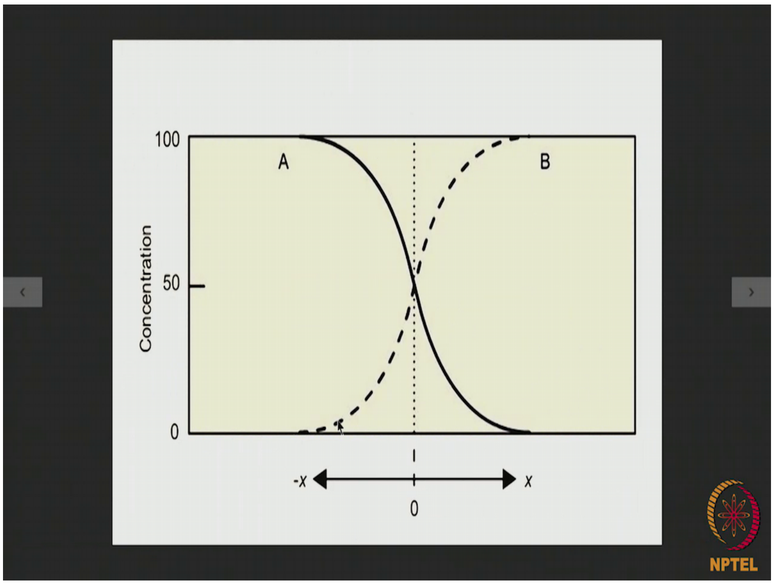

So, this is a very good application of chemical analysis by X-ray absorption now you see the application of this method is possible only when we can have a measurable amount of transmitted intensity and that is the reason why the material to be examined must be very very thin not only that it must have low absorption coefficient that is the reason why in industry nowadays. This method is used only for organic liquids and some other materials which are of low absorption coefficient.